

~~Method for bleaching of a chemical pulp and use of a bleaching solution~~ *BLEACHING OF CHEMICAL PULP WITH PERACID*

5 The present invention relates to a method for the bleaching of chemical pulp, wherein the pulp is treated in a plurality of different steps and a solution containing a peracid is used in at least one of the steps. The invention additionally relates to the use of a peracid-containing bleaching solution in a process step  
10 according to the invention.

In a prior known pulp delignification process, a raw pulp obtained by digesting cellulose-containing materials with suitable digestion chemicals is subjected to a treatment wherein the  
15 lignin is removed and a bleaching which involves the use of oxidative chemicals is carried out. The purpose of conventional bleaching of chemical pulp is to bring to completion the removal of lignin from a raw pulp obtained from a digestion procedure. This bleaching can be carried out by using chlorine or chlorine  
20 dioxide and thereafter alkaline extraction steps in which the lignin is dissolved out of the pulp. At present, the bleaching of a chemical pulp is increasingly often carried out by bleaching methods using no elementary chlorine or chlorine compounds. The first-mentioned bleaching is called ECF (elementary chlorine  
25 free) bleaching and the latter TCF (totally chlorine free) bleaching. The chemical pulp is bleached in several successive steps. Nowadays the bleaching is often started with an oxygen delignification, whereafter further bleaching can be carried out by various methods. In TCF bleaching, delignification can be  
30 continued, for example, by using ozone, peracetic acid or hydrogen peroxide in acid or alkaline conditions. In ECF bleaching, chlorine dioxide steps and thereafter alkaline extraction steps are used.

35 There is a previously known method in which the last bleaching step for chemical pulp is carried out by using peracetic acid.

Peracetic acid can be prepared most simply by mixing vinegar and hydrogen peroxide, whereupon a so-called equilibrium solution is obtained which contains, in addition to peracetic acid, also unreacted initial substances. Also a pure peracetic acid solution can be prepared from this reaction solution by distillation. There are also known other methods for preparing peracetic acid.

Peracetic acid (PAA) is a highly selective bleaching chemical by the use of which good strength properties of the pulp can be maintained. When peracetic acid is used, the optimum pH is approx. 4-7. At a lower pH peracetic acid is a highly selective delignifying chemical. At a higher pH its bleaching action is greater but its selectivity decreases.

By modern bleaching methods, high degrees of brightness can easily be achieved with both ECF and TCF pulps. However, achieving very high degrees of brightness by conventional methods may consume considerable amounts of chemicals. Likewise, after a normal bleaching the variation of the degree of brightness of the pulp and the pH of the stock going to the paper machine may cause runnability problems in the paper machine. Pulp brightness may also be reduced in storage towers, in which case the pulp must be bleached clearly beyond the required degree in order for the reduction of brightness to be compensated for.

A good method for solving these problems is post-bleaching. Agents suitable for post-bleaching include peracetic acid and dithionite. The use of hydrogen peroxide is limited by the fact that in order to function properly it would require alkaline conditions. With respect to pH, dithionite and peracetic acid are highly suited for post-bleaching. Dithionite is used commonly in the bleaching of mechanical pulps, but normally it is not used in the bleaching of chemical pulp. The sulfur present in it may also cause problems. Post-bleaching with peracetic acid is a very effective method of increasing brightness. The consumption of chemicals for bleached pulps is low, and in addition the reaction

is rapid even at low consistency. Furthermore, the optimum pH range for bleaching is precisely suitable for post-bleaching. However, the peracetic acid post-bleaching of chemical pulps involves the problem that, within the pH range optimal for the bleaching result, selectivity is no longer at its best. In the case of a completely bleached pulp having a very low kappa number, the use of peracetic acid damages the fibers, causing the breaking down of carbohydrates and the lowering of pulp strength. This also causes dissolving of organic matter out of the pulp, a factor which may disturb the running of the paper machine.

The bleaching method according to the invention, which solves the problems mentioned above, is characterized in that a peracid is used in the post-bleaching which is the last step of the bleaching process and takes place in the presence of one or more earth-alkali metal compounds. An post-bleaching such as this can advantageously be carried out as a separate step at the paper mill to which the pulp has been transferred from a bleach plant.

The earth-alkali metals, such as magnesium and calcium, used simultaneously with a peracid in the method according to the invention stabilize carbohydrates so that the reducing of the pulp strength is prevented. In other words, the strength of the pulp remains good and the dissolving of organic matter is insignificant. The brightness and whiteness of the pulp are also higher than without the use of earth-alkali metals. This decreases, for example, the need for using optical brighteners in the paper machine. When this method is used, the pH of the stock to be turned into paper, and the brightness and whiteness of the pulp are more even, in which case the runnability of the paper machine is considerably improved.

The adding of magnesium to the pulp, for example in oxygen- and peroxide-based steps, is prior art. Likewise, the use of magnesium in connection with peracetic acid delignification is known from, for example, the publication Liebergott, N., 81st annual

meeting, technical section CPPA (1995), B 157 - B 170. According to the publication, magnesium protects the viscosity of the pulp. The question is, however, of delignification which is carried out on a pulp having a high kappa number. This delignification step is followed by a separate bleaching during which the brightness is raised to its final level. During the delignification, transition metals such as Fe and Mn are released from the pulp, and magnesium prevents their detrimental effects. The addition of magnesium is used for improving the ratio of magnesium to transition metal, which improves especially the running of the subsequent alkaline peroxide step.

In contrast to the foregoing, the invention concerns post-bleaching which is carried out on an already delignified pulp having a low kappa number (preferably below 4) and being free of transition metals, the purpose being to raise the brightness and whiteness of the pulp to the desired level. In this case the peracetic acid turns colorless the chromophoric groups in the pulp, mainly in carbohydrates. In the above-mentioned state-of-the-art methods the question is of the reactions of peracetic acid with residual lignin in the pulp.

Another difference between the prior-art peracetic acid delignification method and the present invention is that in the invention the peracetic acid dose is considerably smaller. In the method according to the invention, surprisingly even a very small peracetic acid dose, 0.1-7 kg/tp, preferably 0.5-3 kg/tp, is sufficient, larger doses being even detrimental.

In methods using peracetic acid known from the literature, it has been observed that the optimum pH with respect to brightness is within a neutral or mildly alkaline range; the strength of the pulp suffers within a slightly acid range. In the method according to the invention it is possible to operate within a pH range of 3-8, preferably 4-7, and at the same the decreasing of the pulp strength is prevented. A preferably acid pH range is

essential for the runnability of the paper machine. It has been observed that by using an earth-alkali metal addition it is possible to carry out post-bleaching within an acid pH range without a loss of pulp strength and without organic matter being dissolved out of the pulp. In prior known methods the best bleaching effect was achieved in mildly alkaline conditions. Since the stability of peracetic acid decreases as the pH rises, when small peracetic acid doses are used wasteful consumption of the chemical decreases brightness. With large peracetic acid doses the effect of wasteful consumption of the chemical does not show. Thus by the method according to the invention it is possible to after-bleach pulp with considerably smaller chemical doses than by prior known methods, without a loss of pulp strength.

Another advantage gained through an post-bleaching carried out using a peracid, e.g. peracetic acid, within an acid pH range is that the acid released during the reaction serves as an acidification chemical, whereupon the use of  $\text{SO}_2$  or  $\text{H}_2\text{SO}_4$  as an acidification chemical is avoided. Thus the total sulfur amount can be lowered and possible  $\text{SO}_2$  odor problems are avoided.

The peracid used in the method is preferably peracetic acid. Other usable peracids include performic acid, perpropionic acid or some longer-chain percarboxylic acid. The peracid may be a so-called equilibrium solution, i.e. a reaction mixture containing the said acid, a peracid and hydrogen peroxide, or a pure peracid solution can be used. The method by which the peracid solution is prepared does not restrict the use of the method; the peracid may be prepared, for example, by distilling an equilibrium solution or from an anhydride and hydrogen peroxide. The peracid may also be a monopersulfuric acid (Caro's acid) or a mixture of Caro's acid and a percarboxylic acid, e.g. peracetic acid. Persulfates may also be used, either as such or as a mixture with any of the above-mentioned peracids.

The earth-alkali metal used in the post-bleaching according to the invention may be in particular calcium or magnesium. These may be added to the bleaching solution in the form of sulfate, acetate, carbonate, oxide or any other compound. It is possible to use in the method either magnesium or calcium alone or both of them together at any ratio. Calcium has over magnesium the advantage that calcium will not precipitate extract-based and resin-based substances which may be present at the wet end of the paper machine.

The post-bleaching according to the invention may be preceded by any known bleaching reaction known from bleaching sequences. The post-bleaching is especially advantageous for use after chlorine dioxide or peroxide bleaching. Also, acidification possibly taking place after the bleaching does not restrict the application of the method; it can be used on both non-acidified and acidified stock. The said acidification may be carried out with, for example,  $\text{SO}_2$ , sulfuric acid or any acid suitable for this purpose. The functioning of the invention is not affected by a possible wash of the pulp before or after the post-bleaching, or by the absence of a wash. The consistency of the pulp to be after-bleached may be 1-30 % and the temperature during the post-bleaching may be between 30 and 100 °C.

The after-bleached pulp may be taken directly to the paper machine or be dried to produce baled pulp.

The method is suited for use on sulfate and sulfite pulps made both from softwood and from hardwood, and on various organosolv pulps.

The said prior art methods in which a peracid and magnesium are used or in which a peracid has been present in the last steps of the bleaching sequence are characterized in that they are carried out in the normal manner in the bleach plant of the pulp mill. The post-bleaching according to the invention, in which the

bleaching reaction is very rapid even at a low consistency, is not tied to the bleach plant and thus also does not require investment in equipment for the bleach plant. As was already pointed out, the invention primarily concerns an post-bleaching carried out after the bleaching sequence of the bleach plant, outside the actual bleaching, for example in the pulp flow pipe during the transfer of pulp, during pulp storage or in the paper machine. Instead of the bleach plant, the place at which the post-bleaching according to the invention is carried out is typically a storage tower for bleached pulp or the paper mill.

The earth-alkali metal compounds used can be added to the bleaching solution in any suitable process step. They can be added to the circulating waters before the water arrives in the post-bleaching step, or they may, for example, come in the dilution waters from the paper machine, where they may be added in any form. It is also possible to use chelators simultaneously with earth-alkali metals.

In addition to the post-bleaching method described above, the invention comprises the use of a solution which contains a peracid and an earth-alkali metal for post-bleaching of delignified pulp at a paper mill.

#### Example 1

A birch sulfate pulp which had been bleached using a sequence consisting of an oxygen step, chelation, an oxygen + peroxide step, a chlorine dioxide step, a peroxide extraction, a chlorine dioxide step (-O-Q-Op-D-Ep-D) was subjected separately to an post-bleaching at 50 °C with a 30 min retention at a consistency of 5 % with a peracetic acid dose of 3 kg/tp at two different pH levels (approx. 6.5 and approx. 4.5). The peracetic acid used had been distilled. Calcium was added to the pulp in the form of acetate, and magnesium in the form of sulfate. The figures in the table indicate the dose of the chemical concerned per one metric

ton of pulp (kg of 100 % chemical/one metric ton of pulp). Experiment number 0 stands for pulp which has not been after-bleached.

5	Exp.	Initial	Final	CaOAc	MgSO <sub>4</sub>	Brightness	Viscosity
	No.	pH	pH	kg/tp	kg/tp	% ISO	dm <sup>3</sup> /kg
	0	-	-	-		90.3	930
10	1	6.5	5.4	-		91.0	766
	2	4.5	4.3	-	-	91.5	845
15	3	6.5	5.3	-	1	92.5	925
	4	4.5	4.2	-	1	92.3	911
	5	6.5	5.4	1	-	92.8	899
20	6	4.5	4.3	1	-	92.6	901
	7	6.5	5.3	0.5	0.5	92.8	887
25	8	4.5	4.4	0.5	0.5	92.5	896

As can be seen from the table, with the earth-alkali addition the viscosity of the pulp can be maintained clearly higher. The viscosity determined by the copper-ethylene diamine method is directly proportional to the strength of the pulp, especially when the same pulp sample is concerned. It is well-founded to assume that the higher the viscosity of the pulp, the better its strength. A higher viscosity also means that the yield is better and that less organic matter has been dissolved out of the pulp.



ISO brightness was improved by approx. 1 % ISO by the earth-alkali addition.

### Example 2

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A birch sulfate pulp which had been bleached by the sequence -O-Q-Op-D-Ep-D according to Example 1 was subjected to an post-bleaching at 50 °C with a 30 min retention at a consistency of 5 % with a peracetic acid dose of 3 kg/tp at different pH levels.

10 The magnesium sulfite addition was 1 kg/tp. The peracetic acid used had been distilled. The brightness of the pulp before the post-bleaching was 90,3 % ISO and viscosity 930 dm<sup>3</sup>/kg.

15		No Mg addition		MgSO <sub>4</sub>	
	Initial	Viscosity	Brightness	Viscosity	Brightness
	pH	dm <sup>3</sup> /kg	% ISO	dm <sup>3</sup> /kg	% ISO
20	3	890	91.4	913	92.0
	3.5	868	91.4	912	92.1
	4	850	91.5	907	92.2
25	4.5	839	91.5	911	92.3
	5	799	91.6	912	92.4
30	5.5	766	91.7	915	92.5
	6.5	750	91.8	925	92.5
35	8	802	91.2	916	91.9

It can be seen from the table that without a magnesium addition the viscosity of the pulp is lowered considerably; at its lowest the viscosity is within a pH range of approx. 5.5-6. Owing to the magnesium addition the viscosity remains high regardless of the pH. Brightness is also clearly higher.

### Example 3

A TCF-bleached softwood sulfate pulp which had been bleached using oxygen, ozone and hydrogen peroxide was after-bleached at 70 °C with a 240 min retention at a consistency of 10 % by using two different peracetic acid doses. The conditions and results of the post-bleaching are shown in Table 3. The brightness of the pulp before the post-bleaching was 86.8 % ISO and viscosity 642 dm<sup>3</sup>/kg, and the kappa number was 1.7.

Experiment No.	1	2	3	4
PAA, kg/tp	3	1.5	1.5	3
pH, initial	7.2	7.2	7.2	7.2
pH, final	6.3	6.6	6.8	5.6
MgSO <sub>4</sub> , kg/tp	1	1	-	-
Residual PAA, kg/tp	0.7	0.5	0.1	0.1
Kappa	1.6	1.6	1.4	1.3
Viscosity, dm <sup>3</sup> /kg	633	625	572	564
Brightness, % ISO	89.1	88.9	88.4	88.6

As is seen from the table, with the magnesium addition a higher brightness was obtained and the viscosity remained clearly better. In post-bleaching with a magnesium addition, no organic matter was dissolved, which can be seen from the kappa number and viscosity of the pulp.

#### Example 4

A TCF-bleached softwood sulfate pulp which had been bleached using oxygen, ozone and hydrogen peroxide was after-bleached at 70 °C with a 240 min retention at a viscosity of 10 % by using two different peracetic acid doses. The conditions and results of the post-bleaching are shown in Table 4. The brightness of the pulp before the post-bleaching was 87.6 % ISO and viscosity 623 dm<sup>3</sup>/kg, and the kappa number was 1.8.

Experiment No.	1	2	3	4	5	6
PAA, kg/tp	1.5	1.5	1.5	1.5	1.5	1.5
pH, initial	7.2	5.5	5.5	6.1	6.5	7.2
pH, final	6.9	4.9	4.9	5	5.5	6.9
MgSO <sub>4</sub> , kg/tp	1	1	-	-	-	-
Residual PAA, kg/tp	0.4	0.4	0.4	0.4	0.4	0.2
Viscosity, dm <sup>3</sup> /kg	612	609	574	571	561	579
Brightness, % ISO	89.9	89.3	88.6	88.5	88.5	89.0

As can be seen from the table, a clearly better final viscosity is obtained with the magnesium addition.

For a person skilled in the art it is clear that the various applications of the invention are not limited to those presented above by way of example only; they may vary within the  
5 accompanying patent claims.